

ITEM V-B CONTINUED FROM FRONT

1. POLLUTANT AND CAS NO. (if available)	2. MARK 'X'	3. EFFLUENT						4. UNITS		5. INTAKE (optional)			
		a. MAXIMUM DAILY VALUE (1) (2)		b. MAXIMUM 30 DAY VALUE (1) (2)		c. LONG TERM AVERAGE VALUE (1) (2)		d. NO. OF ANAL. YRS	e. CONCENTRATION	f. MASS	g. AVERAGE VALUE (1) (2)	h. NO. OF ANAL. YRS	
0. Nitrogen, Total Organic (as N)	X		1.8	102.0					1	mg/L	lbs		
h. Oil and Grease	X		12.8	1,594		3.9	463		1.41	150	806	mg/L	lbs
i. Phosphorus (as P), Total (7723-14-0)	X		0.53	65.0			0.207		22.4		6	mg/L	lbs
1. Radioactivity													
(1) Alpha, Total		X	<14								1	pc/L	
(2) Beta, Total		X	9.4								1	pc/L	
(3) Radium, Total		X	2.1+/-0.62								1	pc/L	
(4) Radium 226, Total		X	1.9+/-1.06								2	pc/L	
k. Sulfate (as SO ₄) (14808-79-8)	X		381	34,000					274	23,282	6	mg/L	lbs
l. Sulfide (as S)	X		0.12	14.3		0.068	6.7		0.03	3.07	161	mg/L	lbs
m. Sulfite (as SO ₃) (14268-48-3)	X		<2	<113.4							1	mg/L	lbs
n. Surfactants	X		0.74	42.0							1	mg/L	lbs
o. Aluminum, Total (7429-90-8)	X		62	5.27					53	3.68	5	μg/L	lbs
p. Barium, Total (7440-39-3)	X		90	5.78					73	4.71	4	μg/L	lbs
q. Boron, Total (7440-42-8)	X		260	17.9					235	15.1	4	μg/L	lbs
r. Cobalt, Total (7440-48-4)	X ^a		<3	<0.26					<3	<0.2	4	μg/L	lbs
s. Iron, Total (7439-89-6)	X		120	10.2					100	6.6	4	μg/L	lbs
t. Magnesium, Total (7439-96-4)	X		18.5	1,242					17.3	1,104	4	mg/L	lbs
u. Molybdenum, Total (7439-98-7)	X		81	4.8					35	2.19	4	μg/L	lbs
v. Manganese, Total (7439-96-6)	X		80	4.74					42.8	2.73	4	μg/L	lbs
w. Tin, Total (7440-31-5)	X ^a		<7	<0.60					<7	<0.46	4	μg/L	lbs
x. Titanium, Total (7440-32-6)	X ^a		<7	<0.60					<7	<0.46	4	μg/L	lbs

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PART C - If you are a primary industry and this outfall contains process wastewater, refer to Table 2c-2 in the instructions to determine which of the GC/MS fractions you must test for. Mark "X" in column 2-a for all such GC/MS fractions that apply to your industry and for ALL toxic metals, cyanides, and total phenols. If you are not required to mark column 2-a (secondary industries, non-process wastewater outfalls, and non-required GC/MS fractions), mark "X" in column 2-b for each pollutant you know or have reason to believe is present. Mark "X" in column 2-c for each pollutant you believe to be absent. If you mark either columns 2-a or 2-b for any pollutant, you must provide the results of at least one analysis for that pollutant. Note that there are seven pages to this part; please review each carefully. Complete one table (all seven pages) for each outfall. See instructions for additional details and requirements.

1. POLLUTANT AND CAS NUMBER (if available)	2. MARK: X ^a a. ANALYST b. DATE c. METHOD d. UNIT	3. EFFLUENT				4. UNITS		5. INTAKE (optional)		
		a. MAXIMUM DAILY VALUE (1) (i) mass	b. MAXIMUM 30 DAY VALUE (1) (i) mass	c. LONG TERM AVERAGE VALUE (1) (i) mass	d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	a. LONG TERM AVERAGE VALUE (1) (i) mass	b. NO. OF ANALYSES	
METALS, CYANIDE, AND TOTAL PHENOLS										
1M. Antimony, Total (7440-38-0)	X ^a	<20	<1.7		<20	<1.3	4	µg/L	lbs	
Arsenic, Total (40-38-2)	X ^{c,d}	21	2.80		15.9	1.69	13	µg/L	lbs	(b)
3M. Beryllium, Total, 7440-41-7)	X ^a	2	0.118		1.25	0.08	4	µg/L	lbs	
4M. Cadmium, Total (7440-43-8)	X ^a	<28	<0.258		<2.4	<0.21	7	µg/L	lbs	
5M. Chromium, Total (7440-47-3)	X ^a	0.03	5.3	0.015	2.4	0.01	1.12	165	mg/L	lbs
6M. Copper, Total (7550-50-8)	X ^c	29	3.02		8.76	0.95	8	µg/L	lbs	(b)
7M. Lead, Total (7439-92-1)	X ^c	13	1.59		8.53	0.810	9	µg/L	lbs	
8M. Mercury, Total (7439-97-6)	X ^a	<0.58	<0.048		<0.6	<0.044	5	µg/L	lbs	
9M. Nickel, Total (7440-02-0)	X ^a	<7	<0.876		6.2	0.527	7	µg/L	lbs	
10M. Selenium, Total (7782-49-2)	X ^c	45	5.3		28.2	2.35	10	µg/L	lbs	
11M. Silver, Total (7440-22-4)	X ^a	<5	<0.425		<5	<0.325	4	µg/L	lbs	
12M. Thallium, Total (7440-28-0)	X ^a	<2	<0.17		<2	<0.13	4	µg/L	lbs	
13M. Zinc, Total (7440-66-6)	X ^c	269	24.0		66.1	5.97	9	µg/L	lbs	(b)
14M. Cyanide, Total (57-12-5)	X	0.019	0.003		0.014	0.002	6	mg/L	lbs	
15M. Phenols, Total	X ^a	0.09	17.9	0.016	3.11	0.01	1.13	482	mg/L	lbs

DESCRIBE RESULTS

All 9 analyses were below detection, as reported on DMRs.

CONTINUE ON REVERSE

CONTINUED FROM THE FRONT

1. POLLUTANT AND CAS NUMBER (if available)	2. MARK 'X'	3. EFFLUENT				4. UNITS		5. INTAKE (optional)					
		a. MAXIMUM DAILY VALUE (if available)	b. MAXIMUM 30 DAY VALUE		c. LONG TERM AVERAGE VALUE (if available)	d. NO. OF ANAL. YRS	a. CONCENTRATION	b. MASS	e. LONG TERM AVERAGE VALUE		d. NO. OF ANAL. YRS		
			(1) mass	(2) mass					(1) mass	(2) mass			
GC/MS FRACTION - VOLATILE COMPOUNDS													
1V. Acrolein (107-02-8)	X	<100					1	µg/L					
2V. Acrylonitrile (107-13-1)	X	<100					1	µg/L					
3V. Benzene (71-43-2)	X	<5					1	µg/L					
4V. Bis (Chloromethyl) Ether (542-88-1)	X	As per 46 Federal Register 2264, this analyte was removed from the Priority Pollutant List.					1	µg/L					
5V. Bromoform (75-26-2)	X	<5					1	µg/L					
6V. Carbon Tetrachloride (56-23-5)	X	<5					1	µg/L					
7V. Chlorobenzene (106-90-2)	X	<5					1	µg/L					
8V. Chlorodibromomethane (124-48-1)	X	<5					1	µg/L					
9V. Chloroethane (75-00-3)	X	<10					1	µg/L					
10V. 2-Chloroethyl Vinyl Ether (110-75-8)	X	<10					1	µg/L					
11V. Chloroform (67-66-3)	X	<5					1	µg/L					
12V. Dichlorobromomethane (75-27-4)	X	<5					1	µg/L					
13V. Dichlorodifluoromethane (75-71-8)	X	<10					1	µg/L					
14V. 1,1-Dichloro-2,2,3,3-tetrafluoroethane (75-34-3)	X	<5					1	µg/L					
15V. 1,2-Dichloroethane (107-06-2)	X	<5					1	µg/L					
16V. 1,1-Dichloroethylene (75-35-4)	X	<5					1	µg/L					
17V. 1,2-Dichloropropane (78-87-6)	X	<5					1	µg/L					
18V. 1,3-Dichloropropylene (542-75-6)	X	<5					1	µg/L					
19V. Ethylbenzene (100-41-4)	X	<5					1	µg/L					
20V. Methyl Bromide (74-83-9)	X	<10					1	µg/L					
21V. Methyl Chloride (74-87-3)	X	<10					1	µg/L					

As per 46 Federal Register 2264, this analyte was removed from the Priority Pollutant List.

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Guidance on metals clean methods and data assessments

May 20, 1993

A two step process must be implemented to effectively improve the quality of trace metals analysis in effluents and receiving waters. The capability and experience of analytical laboratories conducting trace metal analysis particularly with respect to use of trace metal clean methods is varied. Because of this, the first step that any permittee or regulatory agency must take is an evaluation of the sampling, storage, processing and quantification procedures in place presently. The second step is to implement at those laboratories found to be deficient in the use of trace metals clean methods, a more effective program to assure that the introduction of extraneous metals to the sample collection and analysis process is minimized and that control of interferences at the instrument level actively addressed during analysis.

Assessing historical data quality:

1. Evaluating sources of error

The first step is to evaluate the potential for metals to enter the treatment plants by reviewing the sources of metals in the effluent e.g., discharges to the influent stream. If significant metals sources are suspected, high metals concentrations in the effluent may be real. If substantial sources are identified, metals levels should be relatively be low i.e., less than 100 ug/L. Levels frequently will fall in the less than 10 ug/L range. Some metals, such as Hg may be in the sub 0.1 ug/L (<100ng/L) range.

Second, evaluate whether the effluent or receiving water has the potential for significant salt concentrations from intrusions of salt water or other sources into the treatment system e.g., urban run from road salting, etc. If salt is likely to be present in the system, you can be confident that analysts using standard analytical methods are not controlling appropriately for the interferences caused at the instrument level. The only exception will be for samples that are extracted to isolate from the salt or to improve detection limits.

Guidance for evaluating data quality

1. Examine the laboratory QC procedures for

a. Inclusion of method (procedural) blanks and also detection limits appropriate to low level metal measurements (at least 10 times less than the water quality criteria or standard. Procedural blanks must document the sources of contamination and should contribute no more than 10% of to the lowest effluent or receiving water concentration measured.

b. Determination of true procedural or method detection limits. The procedural blanks should be used to evaluate the detection limit for the analytical procedure. MDLs must be determined for the analytical batch being reported not as a general

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detection limit determined at monthly or less frequently intervals. Lowest achievable detection limits are necessary for high quality metals analysis.

c. Matrix spike and certified standard reference materials must be included with each sample batch. The matrix of these standards must approximate that of the being measured and concentrations of these samples must be in the concentration range of the expected (using clean methods) effluent or receiving water. Certified standards in the high ppb range are not acceptable. Recoveries must be within the published variability of the certified value for the analysis to be accepted.

d. Estimates of precision must be included. Both sampling replicates as well as laboratory duplicates must be measured. Greater numbers of replicates will enhance the estimates of variability. Competent labs that have low blanks can usually demonstrate good precision through duplicate analysis. Acceptable variability between duplicates is <20%.

2. Perform sensibility checks on the reported concentrations.

Data should be compared to results collected and reported by laboratories using trace metal clean techniques and known for high quality work to see if the historical data is in a range found for the similar types of receiving waters. If the concentrations are outside of this range, and particularly on the high side, an evaluation of potential source of contamination should be implemented.

3. Evaluation of contamination control procedures.

The steps used to clean labware and storage bottles should be evaluated. Also, control procedures for contamination control during sample collection must be documented. Evaluate if reagents used for acidification or other processing must be appropriate to the low level metal analysis procedures. Reagent grade acids are unacceptable. Hot acid soaking of sample bottles and labware should be part of the contamination control process. Training in clean sample collection methods should be in evidence and documented. If a laboratory can not produce such documentation, sample results are automatically suspect and should not be used. Such simple procedures are not wearing gloves or using gloves with talc during sample collection and sample manipulations will cause poor analytical results.

4. Instrument interferences.

Proper evaluation of potential interferences at the instrument level must be part of the analytical scheme. Proper choice of the acids for sample preservation (Nitric is more acceptable than HCl as it significantly reduces major cation interferences on graphite furnace AAS.) Close matching of the sample matrix (within 10% of the major ion concentrations) to the standards matrix is an absolute necessity for metals analysis when using graphite furnace AAS or ICP measurements. This is particularly important if extraction concentration procedures are not employed for the analysis. Demonstration

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of the match in acids and salt content in the standards versus the sample matrix are critical for identifying potential interferences. Standard addition calibrations may be used if it can be demonstrated that matrixes are closely matched and that the certified values in SRMs are accurately measured.

5. Review of sampling and analysis by experienced researchers

Review of procedures by environmental chemists with demonstrated knowledge in contamination control and instrument interferences is a prerequisite for determining the acceptability of the analytical results. Such individuals should be tasked to review any set of data suspected of being of poor quality. These individuals should look at 5 stages of the analysis.

1. Labware cleaning procedures
2. Sample collection methods and procedures used to control contamination
3. Sample preservation and storage techniques to include the length of time samples are stored prior to processing. The longer the time the cleaner the storage bottles must be and the more stringent the cleanup steps required for successful analysis.
4. Sample processing steps.
5. Instrumental analysis.

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Guidance on the five most critical steps in metals analysis.

1. Labware and cleaning

Is plastic labware used? No other material is acceptable.

Is this plastic ware acid stripped to remove metals from the surface of the material and also subsurface of the labware?

Is there a set of labware dedicated for low level metals measures? Separate sets for receiving water and effluent samples should be maintained.

Is labware air dried in an area free of atmospheric particulate inputs? Use of lab towels or other such materials to dry labware is unacceptable.

Are all surfaces that contact the labware, sampling equipment, storage bottles, etc. washed (dilute acid) frequently and free of particulate materials prior to handling samples.

2. Sample collection/storage

Are metals samples collected as a separate aliquot preferably the first sample from the collection device) and not contacted by any sensor or other procedure used to measure other standard variables i.e., pH, DO, etc.? Sample integrity is an absolute requirement for clean metals analysis.

Use nonmetallic sampling devices (preferably plastic) and samples must be isolated from the atmosphere during collection and processing.

Use acid cleaned (50 degree C, 10% acid solution) labware and storage bottles.

Use acids and reagents of known low metals concentrations. Reagent grade acids are not acceptable except in the initial acid cleaning step of the labware.

Minimize storage times

Preserve samples at pH less than 2, pH 1 for Hg

No testing for standard parameters in the sample prior to sampling for metals or in the metals storage bottle.

Sample bottles must be dedicated to the type of sample e.g. effluent or receiving waters. No cross over of bottles is acceptable.

Sample bottles should be recleaned after use with hot dilute acid (50 degrees C 5% acid)

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3. Sample processing

3a. Filtering

Use acid stripped plastic labware

Use membrane filters only for metals processing; glass fiber is unacceptable.

Use acid cleaned (hot dilute [10%] metal free dilute acids) for at least two days. Change acids and repeat at least once for receiving water filtration.

Filtering on open benches is not acceptable unless the process is completely isolated from atmospheric particulate inputs; filtration must be completed in an area free of atmospheric sources of particulate trace metals.

Minimize sample handling steps and contact with unnecessary labware e.g., pouring sample into a graduated cylinder to measure the volume is not necessary and can add contamination if improperly cleaned.

Dissolved sample receiving flasks or bottles must be cleaned as described above.

3b. Digestion/Preconcentration

Perform total recoverable digestion in a area isolated from atmospheric particulate matter. All processing containers must be protected from extraneous input of particulate matter found in the laboratory. No open beakers, sample bottles, etc. Processing can not occur in metallic hoods as corrosion of the metal parts can contribute significant particulate matter to the sample.

Use acid free reagents. If not commercially available, clean each reagents using chelation or extraction steps. Assume all reagents must be extracted to remove extraneous metals

Verify contribution of metals from each reagent used to process the sample.

Run procedural blanks with solutions of known starting metal concentrations to determine contribution from processing procedures.

4. Instrumental analysis

Check for interfering cations in the sample. Extraction of the sample to isolate the metal from these interferences and at the same time achieve low detection limits is recommended as the procedure of choice.

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Pitfalls of metals analysis

1. Inappropriate method detection limits relative to the water quality criteria.
2. Use of methods intended solely for compliance at water quality standards levels
3. Improper labware and labware cleaning procedures
4. Sampling protocols - improper attention to contamination control e.g. atmospheric input to the sample containers, placement of sampling gear on unclean surfaces., failure to use nontalc plastic gloves
5. Storage protocols - Wrong grade of acids and cleaning of storage bottles
6. Interference control
 - Processing steps
 - Reagent quality
 - Instruments
7. Training in clean methods
8. Improper procedures for determining the procedural blank.

APPENDIX C-2
QA/QC RESULT DATA SHEETS

Table 1

Whiting ETL Wastewater (Outfall 001) - 1/14/94
(Results given in micrograms/liter or ppb)

	12938-75-Total	12938-75-Dissolved
Part B Metals		
Aluminum	49	17
Barium	90	88
Boron	260	260
Cobalt	ND < 3	ND < 3
Iron	130	20
Magnesium	18000	20000
Molybdenum	20	16
Manganese	107	94
Tin	ND < 7	ND < 7
Titanium	ND < 7	ND < 7
Part C Metals		
Antimony	ND < 20	20
Arsenic	14	14
Beryllium	2	2
Cadmium	ND < 2	ND < 2
Chromium	ND < 10	ND < 10
Copper	16	6
Lead	11	ND < 1
Mercury	ND < 0.5	ND < 0.5
Nickel	ND < 7	ND < 7
Selenium	39	38
Silver	ND < 5	ND < 5
Thallium	ND < 2	ND < 2
Zinc	31	23

Re-analysis for total metals: Magnesium = 17600; Manganese = 80; Iron = 80; Copper = 15; Zinc = 25.

Gary R. Chipman
August 17, 1994

Table 2

Whiting Quality Control Samples - 1/14/94
(Results given in micrograms/liter or ppb)

	Field Blank	Trip Blank	Equip. Blank
Part B Metals			
Aluminum	ND < 4	ND < 4	ND < 4
Barium	ND < 1	ND < 1	ND < 1
Boron	ND < 20	ND < 20	ND < 20
Cobalt	ND < 3	ND < 3	ND < 3
Iron	ND < 10	ND < 10	40
Magnesium	ND < 1	ND < 1	22
Molybdenum	ND < 5	ND < 5	ND < 5
Manganese	ND < 1	ND < 1	2
Tin	ND < 7	ND < 7	ND < 7
Titanium	ND < 7	ND < 7	ND < 7
Part C Metals			
Antimony	ND < 20	ND < 20	ND < 20
Arsenic	ND < 1	ND < 1	ND < 1
Beryllium	ND < 1	ND < 1	ND < 1
Cadmium	ND < 2	ND < 2	ND < 2
Chromium	ND < 10	ND < 10	ND < 10
Copper	ND < 3	ND < 3	ND < 3
Lead	ND < 1	ND < 1	48
Mercury	ND < 0.5	ND < 0.5	ND < 0.5
Nickel	ND < 7	ND < 7	9
Selenium	ND < 3	ND < 3	ND < 3
Silver	ND < 5	ND < 5	ND < 5
Thallium	ND < 2	ND < 2	ND < 2
Zinc	ND < 1	ND < 1	5

Analytical Research & Services Division source record numbers: CARN 94-001269 and 94-001536.

Gary R. Chipman
August 17, 1994

Table 3

Whiting ETL Wastewater (Outfall 001) - 2/11/94
(Results given in micrograms/liter or ppb)

	12938-80-Total	12938-80-Dissolved
Part B Metals		
Aluminum	77	23
Barium	68	69
Boron	210	200
Cobalt	ND < 3	ND < 3
Iron	180	10
Magnesium	17000	19100
Molybdenum	20	20
Manganese	34	32
Tin	ND < 7	ND < 7
Titanium	ND < 7	ND < 7
Part C Metals		
Antimony	ND < 20	ND < 20
Arsenic	20	21
Beryllium	ND < 1	ND < 1
Cadmium	ND < 2	ND < 2
Chromium	14	ND < 10
Copper	16	4
Lead	10	ND < 1
Mercury	ND < 0.5	ND < 0.5
Nickel	ND < 7	ND < 7
Selenium	36	30
Silver	ND < 5	ND < 5
Thallium	ND < 2	ND < 2
Zinc	74	27

Re-analysis for total metals: Magnesium = 14600; Aluminum = 62; Iron = 120; Copper = 16; Zinc = 33.

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 August 17, 1994

Table 4

Whiting Quality Control Samples - 2/11/94

	Field Blank	Trip Blank
Part B Metals		
Aluminum	15	13
Barium	ND < 1	ND < 1
Boron	ND < 20	ND < 20
Cobalt	ND < 3	ND < 3
Iron	ND < 10	ND < 10
Magnesium	39	36
Molybdenum	ND < 5	ND < 5
Manganese	ND < 1	ND < 1
Tin	ND < 7	ND < 7
Titanium	ND < 7	ND < 7
Part C Metals		
Antimony	ND < 20	ND < 20
Arsenic	1	1
Beryllium	ND < 1	ND < 1
Cadmium	ND < 2	ND < 2
Chromium	ND < 10	ND < 10
Copper	ND < 3	ND < 3
Lead	ND < 1	ND < 1
Mercury	ND < 0.5	ND < 0.5
Nickel	ND < 7	ND < 7
Selenium	3	ND < 3
Silver	ND < 5	ND < 5
Thallium	ND < 2	ND < 2
Zinc	ND < 1	ND < 1

Analytical Research & Services Division source record numbers: CARN 94-002714 and 94-003103.

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August 17, 1994

Table 5

Whiting ETL Wastewater (Outfall 001) - 3/2/94
(Results given in micrograms/liter or ppb)

	12938-83-Tot	12938-83-Dis	Trip Blank
Part B Metals			
Aluminum	51	26	46
Barium	76	79	ND < 1
Boron	230	240	ND < 20
Cobalt	ND < 3	ND < 3	ND < 3
Iron	100	20	10
Magnesium	18500	19900	50
Molybdenum	19	21	ND < 5
Manganese	31	28	ND < 1
Tin	ND < 7	ND < 7	ND < 7
Titanium	ND < 7	ND < 7	ND < 7
Part C Metals			
Antimony	ND < 20	ND < 20	ND < 20
Arsenic	12	11	ND < 1
Beryllium	ND < 1	ND < 1	ND < 1
Cadmium	ND < 2	ND < 2	ND < 2
Chromium	ND < 10	ND < 10	ND < 10
Copper	18	4	ND < 3
Lead	7	ND < 1	ND < 1
Mercury	ND < 0.5	ND < 0.5	ND < 0.5
Nickel	ND < 7	ND < 7	ND < 7
Selenium	30	25	ND < 3
Silver	ND < 5	ND < 5	ND < 5
Thallium	ND < 2	ND < 2	ND < 2
Zinc	24	17	ND < 1

Analytical Research & Services Division source record numbers: CARN 94-003752 and 94-003946.

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August 17, 1994

Table 6

Whiting ETL Wastewater (Outfall 001) - 3/9/94
(Results given in micrograms/liter or ppb)

	ETL-Total	ETL-Dissolved	Trip Blank
Part B Metals			
Aluminum	62	32	ND < 4
Barium	58	58	ND < 1
Boron	240	240	ND < 20
Cobalt	ND < 3	ND < 3	ND < 3
Iron	100	20	ND < 10
Magnesium	18300	20200	13
Molybdenum	81	73	ND < 5
Manganese	26	24	ND < 1
Tin	ND < 7	ND < 7	ND < 7
Titanium	ND < 7	ND < 7	ND < 7
Part C Metals			
Antimony	ND < 20	ND < 20	ND < 20
Arsenic	16	17	ND < 1
Beryllium	ND < 1	ND < 1	ND < 1
Cadmium	ND < 2	ND < 2	ND < 2
Chromium	10	ND < 10	ND < 10
Copper	18	6	ND < 3
Lead	11	ND < 1	ND < 1
Mercury	ND < 0.5	ND < 0.5	ND < 0.5
Nickel	ND < 7	ND < 7	ND < 7
Selenium	33	31	ND < 3
Silver	ND < 5	ND < 5	ND < 5
Thallium	ND < 2	ND < 2	ND < 2
Zinc	26	18	ND < 1

Analytical Research & Services Division source record numbers: CARN 94-004270 and 94-004582.

Gary R. Chipman
 August 17, 1994

Table 7

Whiting ETL Wastewater (Outfall 001) - 4/14/94
(Results given in micrograms/liter or ppb)

Blank	ETL-Total	ETL-Dissolved Trip	
		11	2
Arsenic	18	ND < 2	ND < 2
Cadmium	ND < 2	5	ND < 3
Copper	10	1	ND < 1
Lead	8	ND < 7	ND < 7
Nickel	ND < 7	16	ND < 1
Zinc	20		

Analytical Research & Services Division source record numbers: CARN 94-006855 and 94-006888.

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August 17, 1994

Table 8

Whiting ETL Wastewater (Outfall 001) - 4/26/94
(Results given in micrograms/liter or ppb)

Blank	ETL-Total	ETL-Dissolved	Trip
Arsenic	13	16	ND < 1
Cadmium	ND < 2	ND < 2	ND < 2
Copper	8	ND < 3	ND < 3
Lead	4	ND < 1	ND < 1
Nickel	ND < 7	ND < 7	ND < 7
Zinc	15	16	ND < 1

Analytical Research & Services Division source record numbers: CARN 94-006781 and 94-006838.

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August 17, 1994

Table 9

**Whiting ETL Wastewater (Outfall 001) Collected during May and June, 1994,
for Arsenic Analysis (Results given in micrograms/liter of ppb)**

Collection Date	Sample No.	ug/L	Arsenic
5/4/94	ETL-001	NA	
	2-N-0		16
	2-N-1		16
	2-N-2		420
	2-N-3		ND <1
5/10/94	ETL-001	18	
	Trip Blank		NA
5/17/94	ETL-001	17	
5/26/94	5-N-0		16
	5-N-1		15
	5-N-2		250
	5-N-3		4
6/1/94	6-N-0		21
6/7/94	7-N-0		13
	7-N-1		12
	7-N-2		433
	7-N-3		ND <1

Analytical Research & Services Division source record numbers: CARN 94-006232, 94-006506, 94-006551, 94-006654, 94-006963, 94-007447, 94-007608, 94-007978, 94-007979, 94-008146 and 94-008318.

**Gary R. Chipman
August 17, 1994**

94230NAP0055

VOLUME I
NPDES PERMIT RENEWAL APPLICATION
FORM 2C ITEM V
FOOTNOTE D

ARSENIC SPECIATION STUDY

Prepared for:

AMOCO OIL COMPANY
Whiting Refinery, Indiana

Prepared by:



August 1994

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FOREWORD

This report is Footnote D to Form 2C, Item V, of Volume I of Amoco's NPDES Permit Renewal application.

The Indiana Water Quality Standards (IWQS) in 327 IAC 2-1-6(a) Table 1 present acute and chronic criteria for trivalent arsenic, i.e., arsenic(III). Arsenic exists as arsenic(III) in a reduced (e.g., low oxygen) environment. Such reducing conditions do not exist in the Whiting wastewater treatment plant (WWTP) process units, the Outfall 001 effluent, or the Indiana waters of Lake Michigan. It should be noted that the total arsenic concentration in Amoco's treated effluent at end-of-pipe, is far less than the allowable federal drinking water concentration for total arsenic.

Amoco has reviewed the arsenic speciation procedures presented in peer-reviewed literature. Amoco has identified a speciation method that yields valid and representative results. The form and species of the arsenic present in the treated effluent from Outfall 001 at the Whiting Refinery have been characterized using this method. Arsenic(III) was not detected in the Outfall 001 treated effluent. This conclusion is consistent with the oxidizing conditions present in the WWTP treatment units, the treated effluent, and the Lake Michigan receiving water. Hence since, arsenic(III) is not detected, the application of the IWQS arsenic(III) criteria to Amoco's renewed permit is not appropriate.

Section 1 contains the introduction to this report. Section 2 presents a review of arsenic water quality criteria established by USEPA and Indiana. Section 3 discusses the environmental chemistry of arsenic and USEPA-approved methods of analyzing total arsenic. Section 4 outlines the development of the arsenic speciation study, including the sampling and analysis program. Section 5 presents the results of the study, and Section 6 presents conclusions drawn from the study.

SECTION 1

INTRODUCTION

Indiana Water Quality Standards (IWQS) set criteria for arsenic(III). Arsenic exists as trivalent arsenic, i.e., arsenic(III), in reduced environments (e.g., low oxygen) but as pentavalent arsenic, i.e., arsenic(V), where oxidizing conditions exist. Any arsenic in the Amoco treated effluent will be in the arsenic(V) species given the oxidizing nature of the WWTP process treatment units and the Lake Michigan receiving water. Lake Michigan water, which is well aerated, is the source of water for the refinery. The application of any arsenic(III) criteria in Amoco's renewed permit would, therefore, be inappropriate for three reasons. First, arsenic(III) should not be present based on the oxidizing environment of wastewater treatment system, the characteristics of the treated Outfall 001 effluent, and arsenic chemistry. Second, sampling and analysis has confirmed that arsenic(III) is not present in the treated effluent. Third, the total arsenic concentration in Amoco's treated effluent, at end of pipe, is far less than the allowable federal drinking water concentration for total arsenic.

FACILITY DESCRIPTION

The Amoco Whiting Refinery includes processes such as distillation, catalytic reforming, hydrodesulfurization, catalytic cracking, alkylation, coking, treating, extraction, dewaxing, grease and lube oil production, asphalt production, sulfur recovery, and power generation. The refining throughput varies with product demand and other market considerations, but its maximum monthly average capacity is 410,000 barrels of crude oil per day. Amoco produces a variety of products including jet fuel, gasoline, diesel fuel, heating fuel, lubricating oils, asphalt, coke and waxes. The refinery generates process waters which are continuously treated onsite at an advanced biological wastewater treatment plant (WWTP). Operation of the activated sludge treatment process requires an aerobic environment at a neutral pH of 6

to 9 s.u. Stormwater run-off and recovered groundwater from refinery areas are also treated at the WWTP. The treated effluent is then discharged to Lake Michigan through a National Pollutant Discharge Elimination System (NPDES) permitted outfall (Outfall 001). Outfall 001 is regulated by NPDES Permit IN0000108 (the NPDES Permit) which became effective on April 1, 1990 and expires on February 28, 1995. The effluent flow from Outfall 001 ranges from 13 (long-term average) to 23 (maximum monthly average) million gallons per day (mgd).

The NPDES Permit has limits for Outfall 001 derived from technology-based effluent limits and historical wastewater treatment plant performance. Amoco has consistently attained these permit limits with high quality effluent that meets or is better than "Best Available Technology" (BAT) effluent limitations. It is anticipated that the new permit will contain effluent limits based on the Indiana Water Quality Standards (IWQS) as well as applicable technology-based standards. As part of the permit renewal application, Amoco is submitting this report to present the results of an arsenic speciation study on the Outfall 001 treated effluent.

It should be noted, as presented in Form 2C, Item V, Part C, that the maximum measured amount of total arsenic in the treated effluent is 21 $\mu\text{g/L}$. This is far below the federal primary drinking water standard for total arsenic of 50 $\mu\text{g/L}$.

STUDY OBJECTIVES

The purpose of this study is to determine whether the IWQS for arsenic(III) applies to Amoco. The objective of this study is to present analytical data to demonstrate the speciation of arsenic in the Outfall 001 effluent. Since there are currently no USEPA-approved analytical